



HAL
open science

Oxidation of Thiophene Derivatives with H₂O₂ in Acetonitrile Catalyzed by [Cp*₂M₂O₅] (M = Mo, W): A Kinetic Study

Marco Ciclosi, Chiara Dinoi, Luca Gonsalvi, Maurizio Peruzzini, Eric Manoury,
Rinaldo Poli

► To cite this version:

Marco Ciclosi, Chiara Dinoi, Luca Gonsalvi, Maurizio Peruzzini, Eric Manoury, et al.. Oxidation of Thiophene Derivatives with H₂O₂ in Acetonitrile Catalyzed by [Cp*₂M₂O₅] (M = Mo, W): A Kinetic Study. *Organometallics*, 2008, 27 (10), pp.2281-2286. <10.1021/om800035f>. <hal-03192597>

HAL Id: hal-03192597

<https://hal.science/hal-03192597v1>

Submitted on 8 Apr 2021

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



HAL Authorization

**Oxidation of thiophene derivatives with H₂O₂ in acetonitrile catalyzed by
[Cp*₂M₂O₅] (M = Mo, W): a kinetic study**

**Marco Ciclosi,^a Chiara Dinoi,^a Luca Gonsalvi,^b Maurizio Peruzzini,^b Eric Manoury,^a
and Rinaldo Poli*^a**

^aLaboratoire de Chimie de Coordination, UPR CNRS 8241 liée par convention à l'Université Paul Sabatier et à l'Institut National Polytechnique de Toulouse, 205 Route de Narbonne, 31077 Toulouse, France; Fax: (+) 33-561553003; E-mail: poli@lcc-toulouse.fr

^b Consiglio Nazionale delle Ricerche, Istituto di Chimica dei Composti Organometallici (ICCOM-CNR) Via Madonna del Piano 10, 50019 Sesto Fiorentino (Firenze), Italy

Summary

The oxidation of benzothiophene (BT), dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (DMDBT) by H₂O₂ to the corresponding sulfoxides and sulfones has been studied under homogeneous conditions in MeCN with compounds [Cp*₂M₂O₅] (M = Mo, **1**; W, **2**) as precatalysts. The W system is *ca.* 100 times more efficient than the Mo analogue, while the relative reactivity of the thiophene substrates is approximately DBT:DMDBT:BT \approx 10:5:1. For all reactions rate constants for both steps (thiophene derivative to sulfoxide, k_1 ; sulfoxide to sulfone, k_2) were measured. While $k_1 \approx k_2$ for DBT and DMDBT, $k_1 \ll k_2$ for BT, independent of catalyst. Activation parameters for the stepwise oxidations of thiophene derivative to sulfoxide (BT to BTO: $\Delta H^\ddagger = 11.4(5)$ kcal mol⁻¹ and $\Delta S^\ddagger = -26.1(1.6)$ e.u.; DBT to DBTO: $\Delta H^\ddagger = 7.7(6)$ kcal mol⁻¹ and $\Delta S^\ddagger = -33(2)$ e.u.) and sulfoxide to sulfone (BTO to BTO₂: $\Delta H^\ddagger = 10.8(5)$ kcal mol⁻¹ and $\Delta S^\ddagger = -21.8(1.6)$ e.u.; DBTO to DBTO₂: $\Delta H^\ddagger = 10.3(9)$ kcal mol⁻¹ and $\Delta S^\ddagger = -25(3)$ e.u.) were calculated from variable temperature studies using [Cp*₂W₂O₅]. DFT calculations suggest that the greater reactivity of DBT relative to BT is not caused by ground state effects but rather by a transition state effect associated with the greater thermodynamic gain in DBT oxidation.

Keywords: Oxidation catalysis, hydrogen peroxide, benzothiophene, dibenzothiophene, 4,6-dimethyldibenzothiophene

Introduction

Sulfur contaminants in transportation fuels represent a major source of atmospheric SO_x, which contribute to air pollution and acid rain, as well as having a poisoning effect on car exhaust catalysts. In order to minimize the sulfur oxide emissions, the desulfurization of crude oil has long been a topic of interest, deep desulfurization being even more critical for the production of fuel-cell grade fuel. Currently, the majority of sulfur is removed by hydrodesulfurization (HDS) technologies,¹⁻⁵ which require high temperatures and high H₂ pressures in the presence of a Mo-based catalyst. Few sulfur compounds, however, are highly resistant to this process and can only be desulfurized slowly under extreme conditions, which raises the cost of the process. Particularly challenging compounds are fused-ring thiophenes, such as benzothiophene (BT), dibenzothiophene (DBT), and their derivatives. 4,6-Dimethyldibenzothiophene (DMDBT), in particular, is one of the most refractory compounds, the steric hindrance generated by the substituents limiting the access to the sulfur atom. Although other techniques have been considered, including selective adsorption⁶⁻⁹ and extraction with ionic liquids,¹⁰ oxidative desulfurization (ODS) combined with extraction is considered as the most promising solution.¹¹⁻¹⁴ Concerning the choice of oxidant, H₂O₂ appears as the best compromise, being more affordable and more environmentally compatible than O₃, NO₂, *tert*-butylhydroperoxide (TBHP) or peracids, and in general more reactive than dioxygen.

Many efficient catalytic systems have been investigated over the last few years and compounds BT, DBT and DMDBT have often been chosen as the model compounds for the activity studies. For obvious reasons of catalyst recovery and recycling, the greatest emphasis is placed on heterogeneous or heterogenized catalysts¹⁵⁻²⁴ and on biphasic approaches using ionic liquids,²⁵ water emulsions^{11, 26-31} or other polar media.³² Nevertheless, useful insights on the reaction may be derived from studies carried out under homogeneous conditions. Studies

of this type require a solvent that is capable of dissolving simultaneously the highly hydrophobic substrates and the oxidant. This has been accomplished with MeCN-H₂O or *t*BuOH-H₂O mixtures^{29, 33} or with neat MeCN³⁴ when performing oxidations with aqueous H₂O₂, or with CHCl₃, CH₂Cl₂, or toluene when using TBHP.³⁵ The investigated homogeneous catalysts include methyltrioxorhenium (MTO),³³ a variety of oxorhenium(V) derivatives,³⁵ an iron system with a tetraamidomacrocyclic ligand,²⁹ and a few Ru(II) bis(phenantroline)-type complexes.³⁴

Some of us have recently carried out extensive studies on the aqueous chemistry of compounds [Cp*₂M₂O₅] (M = Mo, **1**; W, **2**),^{36, 37} which include an improved and simplified synthetic procedure,³⁸ a detailed speciation study for the Mo system,^{39, 40} and the application of **1** to the catalytic cyclooctene epoxidation in CHCl₃ and water.⁴¹ We have now extended our catalytic investigations to the oxidation of the thiophene derivatives BT, DBT and DMDBT with H₂O₂ in MeCN and report here the results of these studies.

Results

The oxidation of benzothiophene (BT), dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (DMDBT) with H₂O₂ was studied in MeCN at various temperatures by use of 1% molar amount of the bimetallic catalyst (*i.e.* thiophene/metal = 50). In most catalytic runs, a H₂O₂/thiophene ratio of 4 was used. The oxidations did not take place to any measurable extent in the absence of catalyst. The gas-chromatographic monitoring in the presence of an internal standard revealed the consumption of the substrates, the formation and then disappearance of the intermediate sulfoxides, and the final formation of the corresponding sulfones as the terminal products. Although different by-products deriving from Diels-Alder cycloadditions may be obtained from simpler thiophene substrates,³³ in the case of BT, DBT and DMDBT no additional peaks from other products

were visible from the GC traces, indicating that the reactions are selective and quantitative. The results of two typical runs, one for BT and the other one for DBT, are shown in Figure 1 for the catalyst **2**. Figures for all other kinetic runs are given as Supporting Information. The reactions took place at a convenient rate for GC monitoring in the 45-75°C range for BT and 15-45°C range for DBT when using the W catalyst. As **1** is much less active than **2**, only one run was carried out with the former for each substrate, at the highest temperature used for the W analogue.

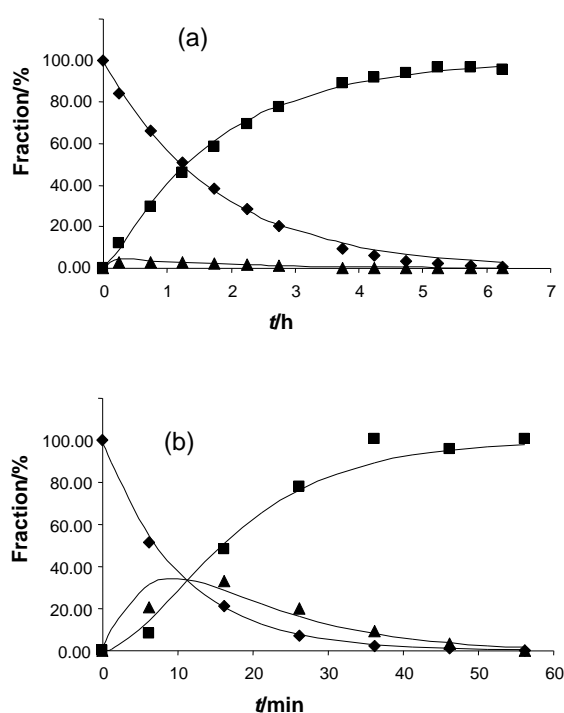
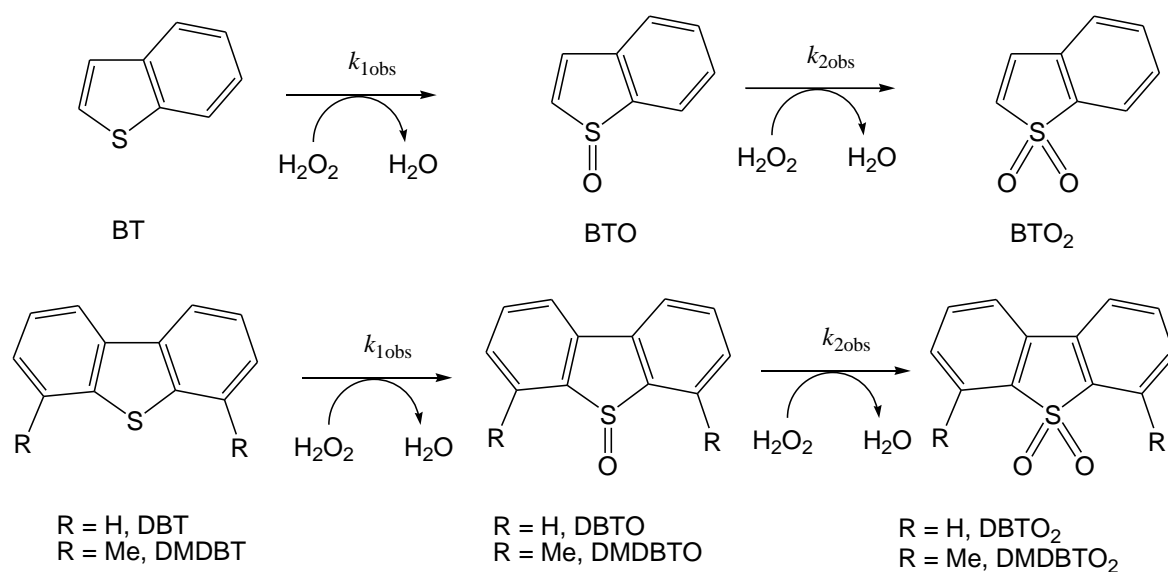


Figure 1. Time dependence of the molar fraction of substrate (diamonds), sulfoxide (triangles) and sulfone (squares) for the oxidation of BT (**a**) and DBT (**b**) catalyzed by **2** using H₂O₂ in MeCN at 45°C. The lines are the corresponding fits (see text).

For DMDBT oxidation, the low solubility of the sulfone hampered a careful kinetics study, especially at the lower temperatures. Even if the reaction was too fast to be monitored by GC at higher temperatures in the presence of **2**, several attempts were made to obtain reliable data using this catalyst in order to compare the relative reactivity of DMDBT and DBT. The best compromise was reached using higher temperature (65°C) and a lower

catalyst loading (0.2%, *i.e.* substrate/metal = 250). Even under these conditions, the sulfone started to precipitate after *ca.* 50% conversion. However, the data collected up to this conversion were sufficient to extract accurate kinetic information.

Observed rate constants were obtained by monitoring the decay of the sulfides ($k_{1\text{obs}}$) or sulfoxides ($k_{2\text{obs}}$) on the basis of two consecutive first order reactions, as indicated in Scheme 1. The values of the observed rate constants are collected in Table 1.



Scheme 1. Stepwise oxidation of BT, DBT and DMBT.

Table 1. Pseudo-1st order rate constants for the two-step oxidation of BT, DBT, and DMBT with H₂O₂ in MeCN catalyzed by [Cp*₂M₂O₅] (M = Mo, **1**; W, **2**).

Run	Substrate	cat	Substr/cat	H ₂ O ₂ /Substr	T (°C)	$k_{1\text{obs}} (\text{s}^{-1}) \cdot 10^4$	$k_{2\text{obs}} (\text{s}^{-1}) \cdot 10^4$
1	BT	1	135	4	75	0.069(1)	2.1(2)
2	BT	2	100	4	75	8.1(2)	151(96)
3	BT	2	100	4	65	4.8(1)	100(36)
4	BT	2	100	4	55	2.56(4)	60(17)
5	BT	2	100	4	45	1.58(2)	31(6)
6	DBT	1	100	4	45	0.235(4)	0.34(1)
7	DBT	2	100	4	45	16(1)	19(2)
8	DBT	2	100	4	35	9.3(4)	9.5(5)
9	DBT	2	100	4	25	6.5(3)	6.5(4)
10	DBT	2	100	4	15	4.0(1)	2.9(1)
11	DBT	2	100	8	35	9.4(2)	7.7(1)
12	DBT	2	100	12	35	5.7(2)	4.3(2)
13	DBT	2	500	4	65	1.92(6)	4.5(3)
14	DMBT	2	500	4	65	0.94(2)	2.2(1)

From an overview of the kinetic data the following trends are observed: (i) catalyst **2** is more active than **1** by a factor of *ca.* 10^2 (*cf.* runs 1 and 2 for BT at 75°C, or runs 6 and 7 for DBT at 45°C); (ii) DBT is oxidized *ca.* 10 times faster than BT in the presence of **2** at 45 °C (*cf.* runs 5 and 7); (iii) for BT, the rate of oxidation of the sulfoxide intermediate, $k_{2\text{obs}}$, is much greater than that of the thiophene precursor, $k_{1\text{obs}}$, by a factor of *ca.* 20 with both catalysts (runs 1-5); (iv) conversely, for DBT the two rates are very similar, once again independent on catalyst (runs 6-13); (v) the DMDBT oxidation is slower than that of DBT, by a factor of *ca.* 2 for both steps (*cf.* runs 13 and 14). Thus, DMDBT shows, like DBT and unlike BT, similar rates for the two oxidation steps.

The DBT oxidation experiment with the W catalyst at 35°C was also repeated with a greater H₂O₂ concentration (twice and three times the amount used in run 8, see runs 11 and 12). The result of run 11 is identical to that of run 8 within experimental error. Tripling the H₂O₂ amount does not increase the rates; on the contrary, a small but noticeable decrease on both rate constants is observed. This change suggests that a lower catalyst concentration is present in run 12. However, this does not appear to result from catalyst decomposition induced by the larger H₂O₂ excess, because the kinetic model of two consecutive 1st order reactions still provide an excellent fit of the data and thus indicates that the catalyst does not significantly change in concentration over the time range of the kinetics experiments. It is possible that equilibria are established by the active catalyst with a larger excess of H₂O₂ to yield inactive or less active metal complexes. At any rate, we can safely conclude that the rate has a first order dependence on the substrate and a zero order dependence on H₂O₂, thus the slow step of the catalytic cycle involves the substrate activation, whereas the activation of H₂O₂ must occur in a faster step.

The question of catalyst stability was also addressed by a separate experiment, carried out under the same conditions of run 8 in Table 1 (catalyst **2**, 35°C, [1] = $8.0 \cdot 10^{-4}$ M;

$[\text{H}_2\text{O}_2]/[\mathbf{1}] = 400$) except for the absence of substrate. UV-visible monitoring shows the complete disappearance of the absorption band within the first 30 minutes. However, upon adding the DBT substrate after a waiting period of 30 min, the catalysis started and proceeded the same rate constants as those reported in Table 1 within experimental error ($k_{1\text{obs}} = 1.01(6)\cdot 10^{-3}$; $k_{2\text{obs}} = 8.4(5)\cdot 10^{-4}$). This experiment proves that compound **1** is not the catalytically active species but merely a pre-catalyst, which undergoes a rapid chemical transformation with H_2O_2 to afford the catalytically active species. The latter, however, appears to be stable under the conditions of the catalysis, even in the absence of substrate. The nature of this catalytically active species will be the subject of further investigations, to be reported in due course.

Another question of stability concerns the oxidant, which is always used in slight excess. Hydrogen peroxide is known to be susceptible to disproportionation with oxygen evolution and some metal complexes are known to catalyze this process. Therefore, it is important to know whether the oxido derivatives used here induce partial oxidant loss during the catalytic run. However, another experiment carried out under the same conditions of that described in the previous paragraph (same conditions as run 8 without substrate), with aliquots periodically withdrawn and titrated iodometrically, reveals a negligible loss of H_2O_2 (ca. 0.5%) over 100 min, *i.e.* a time frame in which the catalyzed oxidation is complete (a plot of the data is shown in the Supporting Information).

The more active W system was investigated at several temperatures for both BT and DBT, allowing the determination of the activation parameters through an Eyring analysis, after conversion of the k_{obs} to the true second order rate constants by dividing k_{obs} by the catalyst concentration (graphs provided as Supporting Information). The resulting parameters are collected in Table 2. The activation enthalpy for the first oxidation process (thiophene to sulfoxide) is almost 4 kcal mol⁻¹ higher for BT than for DBT, whereas the large negative activation entropies (around -30 e.u.) are consistent with an associative mechanism and a very

high level of ordering in the transition state relative to the reactants. The second oxidation (sulfoxide to sulfone) affords similar activation enthalpies for both substrates, similar to the first activation enthalpy of the BT system. The activation entropies are again negative, although not as large in absolute value as those determined for the first oxidation step (around -25 e.u.) and again indicate a relatively ordered transition state. For the DBT system, ΔH^\ddagger_2 is greater than ΔH^\ddagger_1 by nearly 3 kcal mol⁻¹. However, the rates k_1 and k_2 are nearly the same in the studied temperature range, thanks to the less negative activation entropy ($\Delta S^\ddagger_2 > \Delta S^\ddagger_1$).

Table 2. Activation parameters for the oxidation of thiophene derivatives catalyzed by **2**.

Reaction	$\Delta H^\ddagger/\text{kcal mol}^{-1}$	$\Delta S^\ddagger/\text{e.u.}$
BT \rightarrow BTO	11.4(5)	-26.1(1.6)
BTO \rightarrow BTO ₂	10.8(5)	-21.8(1.6)
DBT \rightarrow DBTO	7.7(6)	-33(2)
DBTO \rightarrow DBTO ₂	10.3(9)	-25(3)

Discussion

The current investigation shows that the organometallic compounds [Cp*₂M₂O₅] (M = Mo, **1**; W, **2**) are efficient catalysts for the oxidation of the some of the most resistant sulfur-containing contaminants of crude oil under homogeneous conditions. The tungsten compound **2** shows a much greater activity, *ca.* 100 times higher than that of the Mo counterpart **1** under the same conditions. The greater activity of tungsten compounds relative to the Mo analogues in oxidation catalysis has been noted earlier, especially with respect to epoxidation reactions,⁴² but also in a few instances with specific reference to the oxidation of thiophene derivatives.^{28, 43} The current contribution, however, appears to be the first one to quantitatively assess this difference using homogenous conditions for the oxidation of thiophene derivatives.

The relative reactivity of the three substrates investigated in this study is DBT > DMDBT >> BT, as already reported earlier by use of other catalysts.^{15, 18, 28, 29, 33, 43} However,

other trends have been also described. For instance, DMDBT is more reactive than DBT with the metal-free HCOOH/H₂O₂^{13, 43} and isobutyraldehyde/O₂⁴⁴ oxidation systems and also in other metal-catalyzed oxidations.³² The faster oxidation of DBT relative to DMDBT is consistent with a more important contribution of the steric hindrance of the two methyl substituents located in the 4,6 positions of DMDBT, as these substituents should favour the reaction for electronic reasons where no prior coordination of the substrate is needed. Indeed, the oxidation mechanism is generally considered to involve the addition of the nucleophilic sulfur atom onto the oxygen atom in an activated hydroperoxo (M-O-O-H) or peroxo (M(O₂)) intermediate, thus an electron-rich sulfur atom should be more reactive.

The oxidation of BT, DBT and DMDBT occurs with the formation of the corresponding sulfoxides as observable intermediates, as already reported in previous studies,³³ whereas dialkyl and alkyl-aryl sulfides undergo a first oxidation step (sulfide to sulfoxide) which is much faster than the second one (sulfoxide to sulfone), so that effectively no sulfone is obtained.⁴⁵ One of the most interesting observation of this study is the rate constant trend on going from the first oxidation step (thiophene to sulfoxide, k_1) to the second one (sulfoxide to sulfone, k_2). To the best of our knowledge, there is only one study making such comparison, by use of the Re^{VII} MTO catalyst³³ for the oxidation of various thiophene derivatives, including BT and DBT.

As can be appreciated in Table 3 where these rate constants are summarized for both catalysts, the $k_{1(\text{DBT})}/k_{1(\text{BT})}$ and $k_{2(\text{DBT})}/k_{2(\text{BT})}$ ratios are very similar. In particular, their values indicate a greater reactivity of DBT relative to BT (*ca.* 10 times), whereas the corresponding sulfoxides have approximately the same reactivity. The similarity of these ratios suggests that the two catalysts operate by the same mechanism(s), although the mechanism of the transformation from thiophene to thiophene oxide may be different than that of the second oxidation process.³³ On the other hand, the k_1/k_2 ratios for the same substrate are very different when using a different catalyst. For BT, $k_1 \ll k_2$ when using the W catalyst whereas

the two constants are nearly equal when using the Re catalyst, whereas DBT shows nearly equal rates for the two steps with the W catalyst but $k_1 \gg k_2$ with the Re catalyst. In summary, on going from the W to the Re catalyst, the rate of the first oxidation is increased relative to that of the second oxidation by approximately the same factor for the two substrates. In other words, the Re compound performs better than the W compound as a catalyst for the thiophene to sulfoxide step, whereas the two catalysts perform with similar efficiencies in the sulfoxide to sulfone step.

Table 3. Comparison of rate constants for the first (k_1) and second (k_2) oxidation steps of BT and DBT with the $[\text{Cp}^*\text{W}_2\text{O}_5]$ (in MeCN at 25°C) and $[(\text{CH}_3)\text{ReO}_3]$ (in MeCN-H₂O 1:1, 0.1 M HClO₄ at 25°C) catalysts.

	$[\text{Cp}^*\text{W}_2\text{O}_5]^a$	$[(\text{CH}_3)\text{ReO}_3]^b$
$k_{1(\text{BT})}/\text{s}^{-1} \text{ L mol}^{-1}$	0.053 ^c	1.75(3)
$k_{2(\text{BT})}/\text{s}^{-1} \text{ L mol}^{-1}$	1.2 ^c	1-2
$k_{1(\text{DBT})}/\text{s}^{-1} \text{ L mol}^{-1}$	0.79(4)	21.8(1)
$k_{2(\text{DBT})}/\text{s}^{-1} \text{ L mol}^{-1}$	0.80(5)	0.85(3)
$k_{1(\text{DBT})}/k_{1(\text{BT})}$	15	12.5(2)
$k_{2(\text{DBT})}/k_{2(\text{BT})}$	0.67	0.42-0.85
$k_{1(\text{BT})}/k_{2(\text{BT})}$	$4.4 \cdot 10^{-2}$	$0.85-1.75$
$k_{1(\text{DBT})}/k_{2(\text{DBT})}$	0.99(8)	25.6(9)

^aSecond order k values for the $[\text{Cp}^*\text{W}_2\text{O}_5]$ -catalyzed reactions are obtained by dividing the k_{obs} values in Table 1 by the catalyst concentration. ^bRate constants for the $[(\text{CH}_3)\text{ReO}_3]$ -catalyzed process are from ref. 33. ^cThe rates for the BT oxidation at 25°C are obtained by extrapolation using the ΔH^\ddagger and ΔS^\ddagger values from Table 2.

A question that merits consideration is: why is $k_{1(\text{DBT})} > k_{1(\text{BT})}$, whereas $k_{2(\text{DBT})} \approx k_{2(\text{BT})}$? In the case of DMDBT, both k_1 and k_2 remain close to those of DBT (slightly smaller, both by approximately the same ratio, probably for steric reasons). This comparison is not available for the MTO catalyst, but similar observations have qualitatively been presented (restricted to k_1) for other catalysts.^{15, 18, 28, 29, 43} A common interpretation is that the rate increase with an increase of benzannulation parallels the increase of nucleophilicity of the sulfur atom. However, the addition of a fused benzene ring should not significantly affect the electron density at the sulfur atom, nor the energy of the orbital that is susceptible to electrophilic attack. These propositions seem to be supported by the results of DFT calculations. The computed Mulliken charge on the sulfur atom is positive (in agreement with the low reactivity

of these compounds toward electrophilic reagents) and similar for the two compounds (0.23 for BT and 0.21 for DBT). The orbital diagram for the two compounds, Figure 2, shows an only marginally higher energy for the HOMO, which is the higher-energy Hückel-type orbital with a significant contribution from the sulfur atom, in the case of DBT. The σ -type lone pair of the sulfur atom is located below the highest Huckel-type bonding orbitals (no. 31 for BT, no. 43 for DBT), with an identical orbital energy for both compounds, and is therefore not susceptible to attack by the oxidant. These results are in close agreement with those of previous theoretical studies, which were carried out in relation to the catalyzed hydrodesulfurization process.⁴⁶⁻⁴⁸

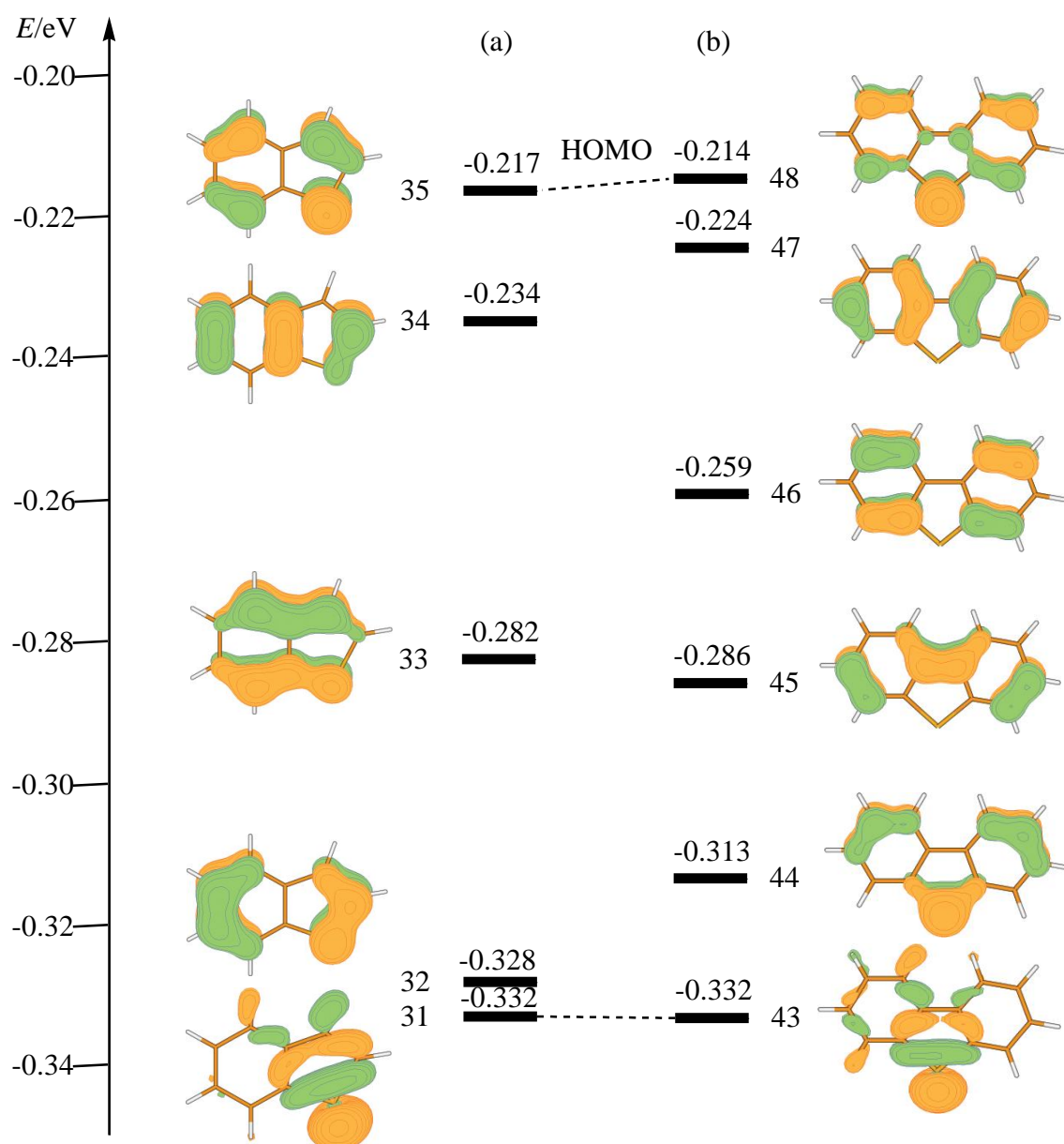


Figure 2. Orbital diagrams for BT (a) and DBT (b).

Thus, if the reactivity difference cannot be explained by a ground state effect, it may be explained by a transition state effect. This effect is most easily examined by looking at the thermodynamics of the reaction. From first principles, it may be expected that the sulfur oxidation removes completely the aromaticity of the thiophene ring, because the sulfur π lone pair is more accessible than the σ lone pair (*vide supra*). Thus, the sulfur atom can no longer contribute two electrons to π delocalization in the oxidation product. The thiophene ring provides a greater contribution to the aromaticity of the less benzannulated system, thus the

thermodynamic gain of the oxidation should be less for BT than for DBT. All these predictions are confirmed by the calculations. As shown in Figure 3, the sulfoxide compounds feature an S-O bond pointing away from the plane that contains the rest of the molecule. The O-S-CNT angle (CNT = thiophene ring centroid) is 127.5° for BTO and 124.8° for DBTO. There is a greater energy gain for the oxidation of DBT relative to BT (by 4 kcal mol^{-1}). This thermodynamic difference is expected, by application of Hammond's postulate, to reflect itself in a greater transition state barrier for the BT oxidation and a lower one for the DBT oxidation. Note that the measured activation enthalpy difference is almost 4 kcal mol^{-1} , very close to the calculated difference in thermodynamics, suggesting that the transition state should very much be product-like. A more detailed computational investigation of the catalytic cycle, or at least of the rate determining step, should be able to confirm or refute this hypothesis.

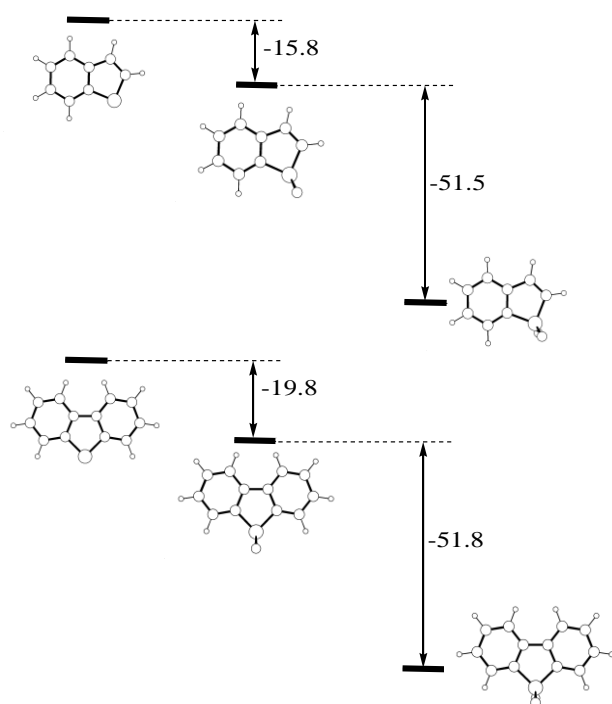


Figure 3. Enthalpy diagrams for the oxidation of BT and DBT to the corresponding sulfoxides and sulfones by H_2O_2 . The reported values are the calculated gas-phase reaction enthalpies in kcal mol^{-1} for the reaction with H_2O_2 , leading to the formation of H_2O .

The calculated thermodynamic gains of the BTO and DBTO oxidations are essentially identical. In addition, the two sulfoxide compounds have sulfur atoms in essentially identical chemical environments and are no longer involved in a delocalized π system. According to the DFT calculations, the Hückel-type bonding orbitals shown in Figure 2 for BT (no. 32-35) and for DBT (no. 44-48) are slightly modified in energy and shape, because of the removal of the sulfur contribution (see details in the Supporting Information). The sulfur σ lone pair (no. 31 for BT and no. 43 for DBT in Figure 2), on the other hand, is raised in energy by the rehybridization process and becomes the HOMO for each sulfoxide compound, with approximately the same orbital energy, see Figure 4. Therefore, the two compounds are expected to display a very similar reactivity toward oxidation, in agreement with the observed approximately identical rate constants with either catalyst.

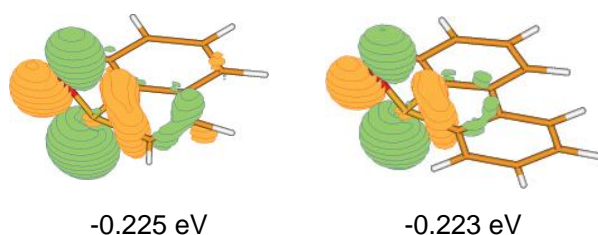


Figure 4. Shape and energy (eV) of the HOMO for BTO and DBTO.

The different effect of the two catalysts on the k_1/k_2 ratios may be a signal that the intimate mechanism of the two steps is different, MTO being a more suitable catalyst for the first step while both catalysts perform equally well for the second one. Coordination of the sulfoxide intermediate to the metal center has been proposed as a possible pathway, whereas the thiophene would directly attack the activated M-O-O-H or peroxide function. More detailed knowledge of the mechanism of each catalytic cycle may be achieved both by model reactions and by computational methods and we plan to operate in that direction. The experimentally determined activation parameters are a benchmark against which the computation method can be calibrated.

Conclusions

The current study has tested the catalytic activity of $[\text{Cp}^*_2\text{M}_2\text{O}_5]$ ($\text{M} = \text{Mo}, \text{W}$) in the oxidation of thiophene derivatives to the corresponding sulfones by use of H_2O_2 in MeCN solution. The W compound is *ca.* 100 times more active than the Mo compound. The greater reactivity of DBT relative to BT does not appear to correlate with a nucleophilicity difference between the two substrates, whereas it correlates with the greater thermodynamic gain associated to the DBT oxidation and this difference is probably reflected by Hammond's postulate at the transition state level. This contribution provides, for the first time, comparative activation parameters (ΔH^\ddagger and ΔS^\ddagger) for the BT, DBT, BTO and DBTO oxidations. These values will be a reference for future computational investigations of the mechanism of the catalytic cycle, the knowledge of which will in turn aid the tailoring of more efficient catalysts.

Experimental section

Materials and instrumentation. The substrates BT (Aldrich), DBT (Aldrich) and DMDBT (Acros), the internal standard 1,3,5-tribromobenzene (Acros) and the oxidant (30% H_2O_2 , Fluka) were used as received. The catalysts, $[\text{Cp}^*_2\text{M}_2\text{O}_5]$ ($\text{M} = \text{Mo}, \text{W}$), were prepared as described in the literature.³⁸ MeCN (SDS, synthesis grade) was used as received. The gas-chromatographic analyses were carried out with a Fisons 8000 Series instrument equipped with a SPB-5 capillary column.

General procedure for the catalytic runs. The reactions were carried out in a Schlenk tube with magnetic stirring, held at the chosen temperature by immersion in a thermostated oil bath. The typical experiment was run by charging the tube with 15 mL of MeCN, followed

by 1.2 mmol of the substrate (BT: *ca.* 161 mg; DBT: *ca.* 221 mg; DMDBT: *ca.* 255 mg), the internal standard (1,3,5-tribromobenzene *ca.* 132 mg, 0.42 mmol) and the catalyst ($1.2 \cdot 10^{-2}$ mmol). The solution was then warmed to the chosen temperature and the aqueous H₂O₂ solution (0.55 mL; 4.8 mmol) was added dropwise. The reaction progress was monitored by gas-chromatographic analysis of periodically withdrawn samples, after quenching the excess H₂O₂ with MnO₂ and filtration. This allowed the independent measurement, for each substrate, of the final sulfone product, the intermediate sulfoxide, and the residual thiophene. Calibration curves could be constructed for the starting thiophenes and for the final sulfones, which were available as commercial products, but not for the sulfoxides. However, the absolute amounts of the sulfoxide intermediate were deduced from the measured gas-chromatographic peak integrals using an arbitrary parameter, which was held constant for all data in any given run. This parameter was optimized, together with the rate constants, during the kinetic fit as two consecutive first order reactions, Scheme 1 (see details in the Supporting Information). The good quality of the fit obtained in each case attested to the suitability of this procedure.

Computational details. All geometry optimizations were performed using the B3LYP three-parameter hybrid density functional method of Becke,⁴⁹ as implemented in the Gaussian03 suite of programs.⁵⁰ The basis functions consisted of the standard 6-31G** for all atoms. All geometry optimizations were carried out without any symmetry constraint and all final geometries were characterized as local minima of the potential energy surface (PES) by verifying that all second derivatives of the energy were positive. All energies were corrected for zero point vibrational energy and for thermal energy to obtain the reaction enthalpies at 298 K. The standard approximations for estimating these corrections were used (ideal gas, rigid rotor and harmonic oscillator) as implemented into Gaussian03.

Acknowledgement

We acknowledge financial support from the European Commission through the AQUACHEM program (contract HPRN-CT-2002-00176), COST (D29 Action) for funding a Short Term Scientific Mission (STMS) of CD in Florence, and the Institut Universitaire de France through a senior membership to RP. In addition, we thank the CICT (through project CALMIP) for granting free CPU time and Mrs. Sandrine Vincendeau for technical assistance with the GC measurements.

Supporting Information Available

Kinetics plots, description of data handling, Eyring plots, molecular orbital correlations for the BT, DBT and corresponding sulfoxides (9 pages).

References

- 1 Grange, P., *Catal. Rev., Sci. Eng.* **1980**, 21, 135-181.
- 2 Topsøe, H.; Clausen, B. S., *Catal. Rev., Sci. Eng.* **1984**, 26, 395-420.
- 3 Chianelli, R. R., *Catal. Rev., Sci. Eng.* **1984**, 26, 361-393.
- 4 Angelici, R. J., *Polyhedron* **1997**, 16, 3073-3088.
- 5 Babich, I. V.; Moulijn, J. A., *Fuel* **2003**, 82, 607-631.
- 6 Yang, R. T.; Hernandez-Maldonado, A. J.; Yang, F. H., *Science (Washington, DC, United States)* **2003**, 301, 79-81.
- 7 Mckinley, S. G.; Angelici, R. J., *Chem. Commun.* **2003**, 2620-2621.
- 8 Mckinley, S. G.; Angelici, R. J., *Energy Fuels* **2003**, 17, 1480-1486.
- 9 Etemadi, O.; Yen, T. F., *Energy Fuels* **2007**, 21, 1622-1627.
- 10 Boesmann, A.; Datsevich, L.; Jess, A.; Lauter, A.; Schmitz, C.; Wasserscheid, P., *Chem. Commun.* **2001**, 2494-2495.
- 11 Collins, F. M.; Lucy, A. R.; Sharp, C., *J. Mol. Catal. A* **1997**, 117, 397-403.
- 12 Bonde, S. E.; Gore, W.; Dolbear, G. E., *Preprints - American Chemical Society, Division of Petroleum Chemistry* **1999**, 44, 199-201.
- 13 Otsuki, S.; Nonaka, T.; Takashima, N.; Qian, W.; Ishihara, A.; Imai, T.; Kabe, T., *Energy Fuels* **2000**, 14, 1232-1239.
- 14 Song, C., *Catal. Today* **2003**, 86, 211-263.
- 15 Wang, D. H.; Qian, E. W. H.; Amano, H.; Okata, K.; Ishihara, A.; Kabe, T., *Appl. Catal. A* **2003**, 253, 91-99.
- 16 Caero, L. C.; Hernandez, E.; Pedraza, F.; Murrieta, F., *Catal. Today* **2005**, 107-108, 564-569.
- 17 Zapata, B.; Pedraza, F.; Valenzuela, M. A., *Catal. Today* **2005**, 106, 219-221.
- 18 Stanger, K. J.; Wiench, J. W.; Pruski, M.; Espenson, J. H.; Kraus, G. A.; Angelici, R. J., *J. Mol. Catal. A* **2006**, 243, 158-169.
- 19 Chica, A.; Gatti, G.; Moden, B.; Marchese, L.; Iglesia, E., *Chem. Eur. J.* **2006**, 12, 1960-1967.

20 Garcia-Gutierrez, J. L.; Fuentes, G. A.; Hernandez-Teran, M. E.; Murrieta, F.;
Navarrete, J.; Jimenez-Cruz, F., *Appl. Catal. A* **2006**, 305, 15-20.
21 Chica, A.; Corma, A.; Domine, M. E., *J. Catal.* **2006**, 242, 299-308.
22 Hulea, V.; Maciuca, A.-L.; Fajula, F.; Dumitriu, E., *Appl. Catal. A* **2006**, 313, 200-
207.
23 Ma, X.; Zhou, A.; Song, C., *Catal. Today* **2007**, 123, 276-284.
24 Wang, Y.; Li, G.; Wang, X. S.; Jin, C. Z., *Energy Fuels* **2007**, 21, 1415-1419.
25 Lu, L.; Cheng, S.; Gao, J.; Gao, G.; He, M.-Y., *Energy Fuels* **2007**, 21, 383-384.
26 Li, C., *et al.*, *Chem. Eur. J.* **2004**, 10, 2277-2280.
27 Huang, D.; Wang, Y. J.; Yang, L. M.; Luo, G. S., *Ind. Eng. Chem. Res.* **2006**, 45,
1880-1885.
28 Komintarachat, C.; Trakarnpruk, W., *Ind. Eng. Chem. Res.* **2006**, 45, 1853-1856.
29 Mondal, S.; Hangun-Balkir, Y.; Alexandrova, L.; Link, D.; Howard, B.; Zandhuis, P.;
Cugini, A.; Horwitz, C. P.; Collins, T. J., *Catal. Today* **2006**, 116, 554-561.
30 Lu, H.; Gao, J.; Jiang, Z.; Yang, Y.; Song, B.; Li, C., *Chem. Commun.* **2007**, 150-152.
31 Huang, D.; Zhai, Z.; Lu, Y. C.; Yang, L. M.; Luo, G. S., *Ind. Eng. Chem. Res.* **2007**,
46, 1447-1451.
32 Al-Shahrani, F.; Xiao, T. C.; Llewellyn, S. A.; Barri, S.; Jiang, Z.; Shi, H. H.;
Martinie, G.; Green, M. L. H., *Appl. Catal. B* **2007**, 73, 311-316.
33 Brown, K. N.; Espenson, J. H., *Inorg. Chem.* **1996**, 35, 7211-7216.
34 Landaeta, V. R.; Gonsalvi, L.; Peruzzini, M., *J. Mol. Catal. A* **2006**, 257, 112-117.
35 Wang, Y.; Lente, G.; Espenson, J. H., *Inorg. Chem.* **2002**, 41, 1272-1280.
36 Collange, E.; Demirhan, F.; Gun, J.; Lev, O.; Modestov, A.; Poli, R.; Richard, P.;
Saurenz, D., *Results and perspectives of high oxidation state organomolybdenum
chemistry in water. In Perspectives in Organometallic Chemistry*, Screttas, C. G.,
Eds., Royal Society of Chemistry: 2003; 'Vol.' 287, p^{pp} 167-182.
37 Poli, R., *Chem. Eur. J.* **2004**, 10, 332-341.
38 Dinoi, C.; Taban, G.; Sözen, P.; Demirhan, F.; Daran, J.-C.; Poli, R., *J. Organomet.
Chem.* **2007**, 692, 3743-3749.
39 Collange, E.; Garcia, J.; Poli, R., *New J. Chem.* **2002**, 26, 1249-1256.
40 Jee, J.-E.; Comas-Vives, A.; Dinoi, C.; Ujaque, G.; Van Eldik, R.; Lledós, A.; Poli, R.,
Inorg. Chem **2007**, 46, 4103-4113.
41 Martins, A. M., *et al.*, *Organometallics* **2005**, 24, 2582-2589.
42 Lane, B.; Burgess, K., *Chem. Rev.* **2003**, 103, 2457-2473.
43 Te, M.; Fairbridge, C.; Ring, Z., *Appl. Catal. A* **2001**, 219, 267-280.
44 Rao, T. V.; Sain, B.; Kafola, S.; Nautiyal, B. R., *Energy Fuels* **2007**, 21, 3420-3424.
45 Vassell, K. A.; Espenson, J. H., *Inorg. Chem.* **1994**, 33, 5491-8.
46 Buemi, G.; Zuccarello, F.; Romeo, G., *THEOCHEM* **1983**, 14, 375-83.
47 Harris, S., *Organometallics* **1994**, 13, 2628-40.
48 Ma, X.; Sakanishi, K.; Isoda, T.; Mochida, I., *Energy Fuels* **1995**, 9, 33-7.
49 Becke, A. D., *J. Chem. Phys.* **1993**, 98, 5648-5652.
50 Frisch, M. J., *et al.*, *Gaussian 03, Revision C.02.* ed.; Gaussian, Inc.: Wallingford CT,
2004.

Table of Contents Entry:

Abstract

Compounds $[\text{Cp}^*_2\text{M}_2\text{O}_5]$ ($\text{M} = \text{Mo}, \text{W}$) catalyze the oxidation of thiophene derivatives to the corresponding sulfoxides and sulfones by H_2O_2 in MeCN. The W system is *ca.* 100 times more active than the Mo system. Activation parameters for both oxidation steps have been obtained for benzothiophene and dibenzothiophene with the W catalyst.

Graphics

